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Origin of anthropogenic hydrocarbons and halocarbons measured in the summertime European outflow (on Crete in 2001)

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Abstract

During the Mediterranean Intensive Oxidant Study MINOS in August 2001, 87 air samples were collected at the ground-based station Finokalia (35°19′ N, 25°40′ E) on the north coast of Crete and subsequently analysed by GC-MS. The analysis includes various hydrocarbons, organo-halogens, HCFCs and CFCs. These compounds have a wide variety of sources and sinks and a large range of atmospheric lifetimes. By plotting the measured variability of these species against lifetime, we found that the compounds describe a linear relationship. It is shown, based on air mass origin analysis and chemical ratios, that several distinct anthropogenic sources influenced the atmospheric composition in Crete. Propane observations are compared to a global model to assess the fossil fuel related emission inventory. Although the model reproduces the general pattern of the propane variations, the model mixing ratios are systematically too low by a factor of 1.5 to 3, probably due to an underestimation of the propane emissions from east European countries in the underlying global database EDGAR. Another important finding was that methyl chloroform, a compound banned under the Montreal protocol, showed significant enhancements from background, which were well correlated with CFC-113. This suggests continued use and emission of methyl chloroform by one or more European countries. We also discuss the observed variations of bromomethane and suggest that the significant peak observed on 12 August 2001 reflects heavy agricultural use as a soil fumigant in Italy.

1. Introduction

Volatile organic compounds (VOC) comprise of a large number of chemical families, including alkanes, alkenes, carbonyls, alcohols, organo-halogens and CFCs. These compounds have a large range of lifetimes from a few hours for pentane to several hundred years for CFC-114.

The most reactive gases (non-methane hydrocarbons – NMHCs- and partly oxy-

ACPD

3, 1893–1923, 2003

genated NMHCs) play an important role in the oxidising capacity of the atmosphere. Their atmospheric breakdown, in the presence of nitrogen oxides, leads to the photochemical build-up of ozone. Therefore, it is essential to determine accurately the budget and distribution of these compounds. While their sinks (mostly through reaction with OH, although the reactions with O_3 and NO_3 can also be significant for unsaturated NMHCs) are quite well quantified by laboratory studies, large uncertainties remain with respect to their sources. These compounds have a wide variety of biogenic sources (vegetation, ocean, etc.) and anthropogenic sources (fossil fuel use and combustion, biomass burning, etc.), for which emissions still need to be confirmed, determined or quantified.

The fact that long-lived species (organo-halogens and CFCs) are radiatively active and that their potential to release chlorine or bromine in the stratosphere leads to ozone destruction, make them important species to study. Following the Montreal Protocol (1987) and subsequent amendments, the production of several halocarbons has now been phased out in developed countries. Several background studies have already reported the expected decrease of these compounds in the atmosphere but, to our knowledge, no measurements have been performed directly in the outflow from eastern Europe to determine the European contribution to their global budgets.

The MINOS campaign on Crete was dedicated to the observation of long-range transport of pollution and presented an ideal opportunity to perform measurements of VOCs in the outflow of eastern Europe and to study their origin. This paper focuses on observations of alkanes (propane, butanes, pentanes) and halocarbons (particularly methyl chloroform, CFC-113 and bromomethane) and discusses their various anthropogenic emissions. A detailed analysis of the oxygenated compounds acetone and methanol is given elsewhere (Salisbury et al., 2003).

ACPD
3, 1893–1923, 2003

2. Experimental

2.1. Site and sampling

Air samples were collected at the atmospheric measurement station Finokalia 35°19′ N, 25°40′ E, 150 m above sea level, a remote site on the northern coast of Crete. Air samples were pressurised in 2.4 L electropolished stainless steel canisters equipped with Nupro SS4H valves, previously flushed with synthetic air and then pressurised to about 3 bar. Using a Teflon membrane pump, canisters were flushed at least 5 times with ambient air and then pressurised to approximately 4 bar. Analysis of the samples was carried out in the laboratory in Mainz between 3 and 6 months after sampling. Stability of the measured compounds over this long period of time has been checked by filling two cylinders with the working standard high-pressure and by measuring them after 1, 3, and 5 months. The working standard was also air collected from Finokalia. For all the compounds presented here but one, no drift in the concentrations was observed and the concentrations remain within the uncertainty range. Exception was chloroform which shown values lower than expected (up to 30%).

In August, the site is influenced by on-shore north-north westerly winds with an average speed of 8 m s^{-1}. The wind advects pollutants from eastern Europe across the Aegean Sea to Crete (see Salisbury et al., 2003, for a complete description of air mass origin). Between 1 and 16 August 2001, 87 air samples were collected at six-hour intervals and at much shorter intervals on selected days.

2.2. Instrumentation

The analytical instrumentation consisted of a gas chromatograph-mass spectrometer system (GC-MS 6890/5973, Agilent Technology, Palo Alto, CA, USA) which has been modified from the commercial version for analysis of low-level ambient air samples. To avoid water related problems (shifting of retention times or ice blocking the trap), water was removed by a magnesium perchlorate trap (replaced approximately every

100 measurements), commonly used for VOC analysis (Namiesnik and Wardencki, 1999 and references therein). Where possible, the lines and the switching valves were incorporated in a heated box (∼50° C). The dryer, which was outside the box, was separately heated to above 75° C to improve drying efficiency and prevent condensation. A known volume of sample (about 1 liter) was cryogenically concentrated at −72° C using a Neslab cc-100 circulation cooler (Portsmouth, USA) at a flowrate of 30–40 ml min^{-1} in a stainless steel microtrap (length: 30 cm, ID: 0.076 cm), packed with porous silica beads (Unibeads 1S, 80/100 mesh, Alltech) over a length of about 10 cm. For GC injection, the cold trap is heated to 200° C in less than 20 s. The carrier gas was Helium (99.9999, with a Supelco®catalytic purifier in-line) at an initial flow rate of 3.7 ml min^{-1}. A 60 m × 0.248 mm DB-5 capillary column (J & W Scientific) was held at −65° C for one minute and then heated to 120° C at a rate of 8° C min^{-1}, followed by ramping to 175° C at a rate of 70° C min^{-1} and remained at this temperature for 5 min before finally being heated at the same rate to 250° C and then maintained at this temperature for 6 min. A complete run lasts about 35 min and allows a good separation of more than 60 identified compounds. The mass spectrometer is operated in single ion mode (SIM) for maximum sensitivity of the measurements. More than half of the samples were measured twice and, on average, the two measurements agreed within 3.5%.

2.3. Calibration and characteristics of the analysis system

Calibrations were performed against a working standard, a 10-L treated aluminium cylinder (Scott Marin, Riverside, California) filled at the Finokalia station two months before the campaign by using a three stage RIX oil-free piston compressor (Mak and Brenninkmeijer, 1994). This cylinder was then calibrated at the National Center for Atmospheric Research (NCAR, Boulder, Colorado) relative to a gravimetrically prepared standard referenced to standards by the National Institute of Standards and Technology (NIST) (estimated accuracy of 2–3%). Two different calibration procedures were used. At first, the mass spectrometer was tuned every week and a calibration was performed several times at the beginning and at the end of a week. It was found that the decrease

of MS sensitivity over the week was almost linear and therefore the response factors for every day were linearly interpolated over the week. However, as the decrease of the sensitivity was significant from week to week, it could not be extrapolated between weeks. Therefore, for the last 37 samples a second method was applied in which the working standard was analysed at the beginning and at the end of the day (the MS still being tuned each week). The average response factor of these two analyses was used to calibrate the samples measured on the same day. There was never a trend in the daily calibration greater than the mean precision which was 15% (see below).

At least two blanks were performed at the start of each measurement sequence and showed a generally clean baseline with only minor impurities of benzene, which were well within its measurement uncertainty.

Several tests were performed in the laboratory to evaluate the characteristics of the analytical system. Detection limits were in the range of 1–10 parts per trillion (10^{-12} mol per mol by volume, pptv) for the compounds reported here. Linearity of the analytical system was better than 3% for all the compounds of interest. Analytical precision of 10 consecutive analyses of the same standard was better than 5% for all compounds except for bromomethane (7%) and methyl chloroform (7%). We estimate the overall uncertainty of the measurements to be better than 15% for all compounds.

3. Results and discussion

Table 1 presents the results obtained for the VOC measurements during the MINOS campaign. The first column gives the overall geometric mean and the corresponding standard deviation. The high standard deviations for the alkanes are due to the large variability of their mixing ratios between clean and polluted events (see Sect. 3.2.1). In contrast, the CFC's which have longer lifetimes show less variability and hence lower standard deviations. For comparison with other studies, the average value observed on 7 August is included and indicated as "clean air" (Table 1). This day was the least influenced by recent pollution as indicated by the relatively low values of all measured

hydrocarbons (e.g. alkanes and benzene).

3.1. Relationship of variability and lifetime of compounds

The lifetimes of VOC measured during MINOS vary between about 0.6 days (pentane) and 300 years (CFC-114). It has been shown previously that the variability of a compound and the measurement site are related to the sources and sinks of the compounds (Jobson et al., 1999; Jobson et al., 1998; Junge, 1974; Williams and al., 2000). Jobson et al. (1998) showed empirically that the variability and lifetimes of hydrocarbons can be linked through the equation $SlnX = A\tau^{-b}$. SlnX represents the standard deviation of the logarithm of the mixing ratio of hydrocarbon X, τ is the chemical lifetime of the hydrocarbon and A and b are empirical fitting parameters. Jobson et al. (1999) extended this study by examining the variability/lifetime relationship for a larger number of VOC (hydrocarbons and halocarbons). From these studies, it was proposed that the coefficient b, the dependence of variability on lifetime, reflects the importance of the source/sink budget in the regional variability of the studied species and varies from b=0 being close to the sources to b=0.5 in remote locations. Since these first studies, the variability concept has been applied to a number of datasets and has proved useful in ascertaining the consistency and quality of measurements and for the estimation of OH concentrations (Williams and al., 2000; Williams et al., 2001, Karl et al., 2001). The variability concept is based on the assumption that the chosen compounds have, more or less, the same source distribution. As a first, rough iteration, this is the case for the compounds reported in this paper, which are mostly of anthropogenic origin. Methyl chloride and bromide are exceptions, as they have a globally important oceanic source.

The relationship between the variability and the lifetime of the VOC measured during the MINOS campaign is shown in Fig. 1. The lifetimes of the reactive compounds were estimated by using the average measured OH value of 4.7×10^6 molecules cm^{-3} (Berresheim et al., 2003) and by assuming that OH is the only significant sink of these compounds. For the long-lived compounds, we used the global mean lifetimes as given

by Jobson et al. (1999). A linear relationship of the form SlnX = 0.85 $\tau^{-0.23}$ (R=0.96) was observed (Fig. 1). Note that the derived b coefficient is not sensitive to OH within the measurement uncertainty of OH (±30%). The fact that methyl bromide and chloride lie almost on the line may indicate that their anthropogenic emissions govern their variability in this region. However, this cannot be determined unequivocally from the variability plot.

The coefficient A, which relates to the range of air mass ages, is low (0.85), suggesting a narrow distribution of air mass ages. This is consistent with the range of the air mass ages estimated with toluene:benzene ratios (15–35 h, Salisbury et al., 2003) and ethylbenzene/acetophenone ratios (15–59 h, Xu et al., 2003). The coefficient b of this study has an absolute value of 0.23 and is significantly lower than the value of ∼0.5 found during PEM-West B and at Amsterdam Island in the Indian Ocean (Jobson et al., 1999; Williams et al., 2001) but higher than the value of 0.18 found for the Harvard Forest site (Jobson et al., 1999). This suggests that Finokalia represents intermediate conditions between remote sites (where the variability is strongly dependent on the lifetime) and sites in the vicinity of sources (where sources dictate the variability, not the chemistry). In addition, the relatively quite high scatter observed on the plot suggests a wide variety of sources which are discussed further below. This is consistent with the back-trajectories analysis, which showed that several regions in Europe, and particularly in eastern Europe, have influenced the air composition of Crete during the MINOS experiment (Salisbury et al., 2003).

In order to characterize the anthropogenic sources influencing the observations during MINOS better, the next sections will be dedicated to more detailed analyses of some specific compounds.

3.2. Fossil fuel and biomass combustion

3.2.1. Temporal variations of propane

Figure 2 presents the propane volume mixing ratios observed during the MINOS campaign (the propane values calculated with the global model MATCH are also presented on this graph and will be discussed in the next section). The classification of time periods is based on the variations of CO, BC and other compounds, and on back-trajectories calculations. More details about the definition of these periods can be found in Salisbury et al. (2003) and only a brief summary is given here. During period 1 (no VOC measurements during this period), air originating in Eastern Europe was observed. During period 2, the air originated above the boundary layer in Western Europe and was advected approximately east-south-east before descending and turning south-west over the Black Sea and north-western Turkey. Period 3 corresponds to a highly polluted event, mainly due to biomass burning emissions, originating from eastern Europe. Finally, period 4 corresponds to mixed trajectory origins, associated with some regional influence. Although some scatter is associated with the data, propane variations signify the air mass changes between periods. In period 2, the lowest values of propane (~120 pptv) were observed. This is consistent with photochemically aged air descending from the free troposphere without recent contact with pollution sources. During period 3, significantly enhanced propane mixing ratios (up to 500 pptv) were observed, consistent with the corresponding high levels of CO and BC which have been attributed to the influence of biomass burning by reference to acetonitrile. We note that chloromethane and benzene, two compounds emitted by biomass burning, presented large enhancements (up to 40% for chloromethane and to a factor of 6 for benzene) during this period. The transition between period 3 and 4 is characterized by average levels of propane (~200 pptv) which reach high concentrations (up to 750 pptv) during period 4, consistent with some regional influence which was also evident from other compounds. Propane shows a large degree of scattering during period 4, reflecting

ACPD
3, 1893–1923, 2003

the mixed origin of the air during that time.

3.2.2. Comparison with the global model MATCH

Figure 2 also shows the propane mixing ratios calculated by the MATCH-MPIC chemistry-transport model (Model of Atmospheric Transport and CHemistry – Max Planck Institute for Chemistry version). MATCH is a global atmospheric offline model, which can be driven by different meteorological datasets. Here the National Center for Environmental Prediction (NCEP) meteorological data at a horizontal resolution of about 2.8° × 2.8° with 42 levels are used. MATCH is driven by meteorological parameters from the air mass trajectory re-analysis (Lawrence et al., 2002). The chemical scheme includes $CH_4 - CO - HO_x - NO_x$ "background" chemistry, a simplified representation of isoprene chemistry, explicit ethane (C_2H_6) chemistry along with simpler representations of propane (C_3H_8), ethylene (C_2H_4), propylene (C_3H_6) and n-butane (C_4H_{10}) chemistry. The latter species is used as a surrogate for all higher alkanes. A complete description of the model can be found in Lawrence et al. (1999), von Kuhlmann (2001), von Kuhlmann et al. (2002a) and references therein and comparisons with the MINOS flight data are given in Lawrence et al. (2002). As propane is treated specifically, it is therefore the measured organic species most appropriate to directly compare with the model.

The model reproduces the main features observed during the campaign quite well, especially showing higher levels of propane during periods 3 and 4 and lower levels during period 2 and during the transition between period 3 and 4. However, the simulated mixing ratios of propane are lower than the observed data by a factor of 1.5 (background conditions) to 3 (polluted event observed in period 4).

The deviation between the modelled concentrations and our observations might have various sources, ranging from measurement errors, local influences in our measurements, erroneous modelling of eastern Mediterranean meteorology or inaccuracies in the emission data. We can rule out the first hypothesis as the uncertainty in the measurements, estimated to be lower than 15% (Sect. 2.3), cannot account for the

ACPD
3, 1893–1923, 2003

observed discrepancy between model and measurement. Local source influences did not cause the difference as well; based on our interpretation of Fig. 1 (Sect. 3.1), the Finokalia site is hardly affected by local sources. Finally, errors in the model calculation are most likely not responsible for discrepancy between model and measurement results: the model captures well the main variations of propane observed during MINOS, which indicates that the meteorology and the chemistry used in the model are realistic. Also, the modelled CO is very well correlated (r = 0.73) with the flight data (Lelieveld et al., 2002). Therefore, an underestimation of the propane emissions used in the model is the most likely reason for the discrepancy. We note that propane concentrations simulated with the MATCH model were already compared to propane observations at several locations and that a reasonable agreement was found for northern Europe while an underestimation by a factor of 2 was found over North America (von Kuhlmann et al., 2002b). The discrepancy between measurements and model is therefore regionally dependent, which is consistent with the hypothesis that the problem comes from the emissions database. We will now dedicate the next section to discuss the propane emissions used for the MINOS comparison.

3.2.3. Emissions of propane

The propane emissions used in the model calculations are compiled by von Kuhlmann et al. (2002a). Emissions from energy and industrial activities have (except for biofuel emissions) been taken from the Emission Database for Global Atmospheric Research (EDGAR v2.0, Olivier et al., 1996; Olivier et al., 1999a). Biomass burning emissions (including biofuel) have been included by von Kuhlmann et al. (2002a) based on emission factors presented by Andreae and Merlet (2001). These emission factors were used to calculate a propane/CO emission ratio (biomass burning) per type of biomass which has been used to scale the CO emission distribution of Galanther et al. (2000). Together with emissions from the energy/industry system (5.4 Tg), biomass burning emissions (1.7 Tg) account for 95% of the global budget of 7.4 Tg.

The discrepancy between model and observations is observed for the whole cam-

paign, including the beginning of the campaign where biomass burning influence was very low (Salisbury et al., 2003). Therefore, we will focus on possible errors in the energy/industry emission estimates and we will discuss successively four points: i) total VOC estimates, ii) speciation of the VOCs, iii) seasonal variation and iv) importance of the year of the simulation.

i) In EDGAR, the total NMVOC (non-methane volatile organic compounds) emissions have been calculated using an emission factor approach. This emission might be inaccurate due to poorly known emission factors or activity data. In Olivier et al. (1999b) the uncertainty of the NMVOC emissions is estimated to be "medium" (50%) for fossil fuel related emissions and "large" (>100%) for non fossil fuel emissions.

ii) The calculation of propane emissions in EDGAR are based on the application of sector-fuel specific NMVOC profiles which assign the fraction of each of 25 different NMVOC compounds from the total NMVOC emission. An inaccurate speciation of the compounds could also lead to a wrong estimation of propane emission. However, a calculation performed on the ratios of butanes/propane and pentanes/propane observed during MINOS suggests that the speciation provided by EDGAR is consistent with our measurements (see Sect. 3.2.4). This would further suggest that butane and pentane emissions are also similarly underestimated in the EDGAR database.

iii) A third possible source of inaccuracy in the emission figures is that the energy/industry emissions are provided as total annual emissions. This means that the total propane emission was distributed uniformly over the year so that temporal variations such as seasonal changes or particular emission events are not taken into account.

iv) Finally, the MATCH model simulation was performed with EDGAR v2.0 emission values that are representative for the year 1990. A detailed propane emission inventory for more recent years is not available at the moment. The question arises

if and to what extent emissions of propane within the study domain have increased over the period 1990–2001. An indication of a possible increase in propane emissions can be found when looking at the recently constructed EDGAR v3.2 emission inventory. This inventory presents for total NMVOC (not speciated) an update of 1990 emissions and an estimate of 1995 emissions. For countries that have a large influence on the MINOS observations (Greece, Turkey and Ukraine) the NMVOC emissions according to EDGAR v2.0 and EDGAR 3.2 are presented in Table 2. The results for total NMVOC show both a systematic error in the calculation of Ukrainian emissions in version 2.0 and that emissions for more recent years (1995) are a factor 3.5 higher than the Ukrainian emissions used in the model calculations. For Greece and Turkey some small difference can be found. If this difference in total NMVOC emissions is also found in the propane emissions then the discrepancy between model and observation can probably be explained by an underestimation of propane emissions in the Ukraine and maybe in other countries from the former Soviet Union. This could not be verified since EDGAR v3.2 propane emissions are not available yet. The discrepancy between v3.2 and v2.0 for the year 1990 can largely be explained by the fact that in v2.0 Ukrainian emissions were calculated based on statistics from the total former Soviet Union which were scaled to sub-regions based on e.g. population distributions. However, statistics have been revised in the past years, new sources were added and emission factors were revised for some sources. During the construction of v3.2 country specific energy and industry statistics were available for the Ukraine (J. G. J. Olivier, personal communication).

3.2.4. Photochemical processing of the alkanes observed during MINOS

Assuming Lagrangian transport and assuming that the only process affecting the ratio butane/propane (pentane/propane) since the emission is the reaction with OH, one can

easily derive the evolution of these ratios with time, as follows:

$$[A]_F/[B]_F = [A]_S/[B]_S \times \exp((k_B - k_A) \times [OH] \times \Delta_t) \quad (1)$$

with [A] mixing ratio of the compound A, the subscripts F and S stand for Finokalia and emission source region, respectively. k_A: reaction rate of the compound A with OH, [OH]: OH concentration, and Δ_t: transport time.

Ratios of butanes/propane and pentanes/propane were considered for this calculation. For comparison with the categories defined in the EDGAR database, iso and n-butane were aggregated in butanes and iso- and n- pentane in pentanes and the average reaction rate was considered (Baulch, 1986; Donahue et al., 1998). Emissions of the alkanes were extracted from the EDGAR database (Olivier et al., 1996) for Greece, Turkey and Ukraine, three countries which likely had the most influence on the observations performed during MINOS. The values reported for Finokalia represent the average of the ratio (and its standard deviation) for the first part of the campaign (until end of period 2). Only the first part of the campaign has been considered to exclude periods which were affected by different emissions (nature of the emission and/or geographical origin of the emission). The concentration of OH was taken as the mean value measured during periods 1 and 2 (4.0 10^6 molecules cm^{-3}, Berresheim et al., 2003). Finally, transport times of 24 h and 48 h were considered to cover the range estimated by using toluene:benzene (Salisbury et al., 2003) and ethylbenzene/acetophenone ratios (Xu et al., 2003) for the corresponding periods.

Butane/propane and pentane/propane ratios at the emission point, after chemical processing (24 h and 48 h) and observed at Finokalia are shown in Table 3. Keeping in mind the limitations of this rough calculation, one can note that emissions from Turkey and Ukraine probably influenced the observations made during the first part of MINOS most strongly. Indeed, both observed ratios (butane/propane and pentane/propane) are consistent with emissions from these countries and transport times ranging from 24 h to 48 h.

Comparing our observations with the few other measurements of hydrocarbons performed in non-urban areas of Greece shows that the mixing ratios were in the same

absolute concentration range for the C3–C5 hydrocarbons (Bonsang et al., 1999, Moschonas, 2000). However, we note that the VOC ratios were different in all three campaigns, reflecting different emission sources (the other studies were performed over continental Greece, and were certainly more affected by Greek emissions) and different extent of photochemical processing.

3.3. Anthropogenic solvent emission

3.3.1. Temporal variation of methyl chloroform

Methyl chloroform (1.1.1. trichloroethane) has been widely used over the last 40 years as a solvent. However, its capacity to release chlorine in the stratosphere (leading to ozone destruction) has led to the phasing out of its production. This phasing out, initially planned for 2005 (Montreal protocol and London amendment), has been brought forward to 1996 for developed countries (Copenhagen amendment) (McCulloch and Midgley, 2001). Therefore, methyl chloroform (MCF) emissions are now considered to be almost zero for mid-latitude countries in the northern hemisphere. The measured methyl chloroform mixing ratios during MINOS are shown in Fig. 3 and show large peaks on 5, 9 and 14 August. Since biomass burning is a small source of MCF (Rudolph et al., 2000), the observed simultaneous enhancements of CFC-113 indicate that other anthropogenic sources were causing the MCF peaks observed during MINOS (Fig. 3). The good correlation (R^2=0.5 for the whole campaign) observed between MCF and CFC-113 (CCl_2FCClF_2), whose applications are similar to those of methyl chloroform, clearly indicate that significant emissions of these compounds still occur in Europe.

These peaks cause the relatively high variability of MCF, which pulls its value above the linear fit line in Fig. 1. If emissions would have ceased, MCF should be below the line defined by species that still have source generated variability, as was clearly observed in data collected in the remote southern Indian Ocean (Warneke and de Gouw, 2001).

Finally, one should note that the increase of methyl chloroform and CFC-113 which is observed during period 3 clearly indicates that the large pollution event attributed to biomass burning emissions (Salisbury et al., 2003) also included some other anthropogenic emissions, at least on 9 August. In addition, a peak in propane was observed on 14 August which was not the case on 9 August. This likely indicates that the two events did not have the same source origin, which suggests that the significant methyl chloroform enhancements on 9 and 14 August may have originated in different countries.

3.3.2. Emissions strength of methyl chloroform

To evaluate the origin of the methyl chloroform emissions, we used an atmospheric-tracer transport model which allows studying the European region with a horizontal resolution of 1° by 1°. Vertically, 25 layers are used, which are mostly located in the boundary layer and in the free troposphere. The reference simulation of the model considers a total emission of 1 Tg/year methyl chloroform for Europe. Sensitivity simulations were performed by considering an additional methyl chloroform source (equivalent to 10 Tg/year) for the different European countries whose emissions may have influenced observations in Crete (Krol et al., 2003). The only exception to this procedure was for continental Greece, where the enhancement was only of 1 Gg/year (otherwise its proximity to Finokalia would lead to an unrealistically large impact). The results shown in Fig. 4 demonstrate that the main source of MCF observed at Finokalia on the 5 August would have been from Turkey, with possible contributions from Bulgaria and Greece while the 9 August event corresponds to possible impacts from both Turkey and Ukraine (this last country signed the Copenhagen amendment in April 2002). The increase of methyl chloroform observed on 14 August could be attributed to Ukraine, but also to Bulgaria or Romania. It should be noted that contributions from the Caucasus region (not included in this simulation), where high levels of MCF were already observed (Folberth et al., 2000, 2003), can not be excluded.

3.3.3. Implication for OH calculation

Methyl chloroform has received much attention recently because its known anthropogenic emissions could help to indirectly determine global mean OH concentration and trend (Spivakovsky et al., 2000; Prinn, 2001; Krol and Lelieveld, 2002 and references therein). Recently, Prinn (2001) derived a strong negative trend of OH over the last decade, based on the assumption that emissions of MCF have ceased. However, during MINOS and other experiments performed in Europe (Krol et al., 2003), it has been shown that significant methyl chloroform emissions still take place in some parts of Europe. Therefore, the uncertainty on the current MCF emissions makes any conclusion on OH distribution and trend difficult. In particular, the previously derived trend is probably exaggerated and tropospheric OH may have been relatively constant over the last decade (Krol et al., 2003).

3.4. Anthropogenic agricultural emissions (bromomethane)

The bromomethane (CH_3Br) measurements are shown in Fig. 5 along with the previously discussed propane results. Along with its natural source from the ocean, bromomethane is emitted by biomass burning, produced industrially and used for agricultural purposes (Schauffler et al., 1999 and references therein). Fumigation of soils before planting is the largest single use of CH_3Br worldwide (over 80%, Lee-Taylor et al., 1998). We note on Fig. 5 three noticeable features that we will thereafter briefly discuss.

At first, values observed on 7 August (defined as a “clean” day) are slightly higher than the overall mean (see Table 1). This is due to the definition of the “clean” period, which was chosen as the day the least influenced by recent pollution based on the low values of fossil fuel derived hydrocarbons measured that day. Due to the longer lifetime of bromomethane, some older polluted air masses could still contain elevated concentrations of CH3Br. Alternatively, the fact that CH_3Br has specific anthropogenic sources resulting from agricultural activity could also explain this feature.

Secondly, although biomass burning is estimated to contribute about 15% to the global budget of CH3Br (Lee-Taylor et al., 1998), no significant enhancement of this compound is observed during the polluted event of period 3 where biomass burning influences predominated. We note that considerable variability in the emission ratios of CH_3Br emitted by biomass burning processes has been observed, depending strongly on the bromine content of the fuel and on the proportion of flaming to smoldering combustion (Andreae and Merlet, 2001). We further note that CO, a compound emitted mainly during the smoldering phase, was significantly enhanced during this event. Therefore, the fact that we observe no significant signal of CH_3Br during period 3 suggests that the monitored biomass burning event was associated with a low-bromine content fuel.

Finally, although most of the measurements lie between 10 and 15 pptv, one noticeable peak of CH3Br can be observed on 12 August, with two values higher than 25 pptv, which then progressively decrease to 13 pptv (16 h after the maximum). This peak is significant with respect to instrumental uncertainty and indicates that this compound is being emitted. As no other measured VOC shows a concomitant increase, this peak of bromomethane likely reflects the influence of a specific source of this compound. According to Fig. 4, which shows the sensitivity of the measurements to the emission regions, a large contribution from south/north Italy is observed on 12 August. As Italy is the largest consumer of CH_3Br as soil fumigant in Europe and the third most important worldwide (ICF, 1997 and references therein), it is plausible that this specific source of bromomethane is responsible for the higher levels observed on 12 August.

4. Summary and conclusions

The MINOS campaign provided a good opportunity to investigate the anthropogenic origin of several VOC from European sources, in particular from southern and eastern Europe. By studying the variations observed during the campaign, we have derived information about the anthropogenic emissions of propane, methyl chloroform

and bromomethane. Propane, mainly emitted by fossil fuel and industrial processes, was compared with the simulated propane from the global model MATCH. While the model reproduces the general features of propane variations quite well, it underestimates significantly its mixing ratios, which is attributed to an underestimation of the emissions (provided by the global database EDGAR). Initial investigations suggest that the total amount of VOC accounted for in the database in some countries is too low but further research is needed to address this issue. Emission inventories urgently need updating if models are to be compared with measurements.

Special attention was also dedicated to the interpretation of the methyl chloroform measurements, as some unexpected deviations from the background were observed during MINOS. This observation, complementing other measurements in Europe, shows that methyl chloroform emissions still occur in Europe. These emissions need to be precisely quantified if the method of OH estimation (distribution and trend) based on methyl chloroform is to be further applied.

Bromomethane measurements indicate that no significant regional biomass burning sources were detected. Variations of CH_3Br were not associated with fossil fuel usage but with a specific source region (Italy) and most probably associated with agricultural fumigant usage.

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Table 1. Average mixing ratios of selected VOC measured during MINOS

	Overall air ppt	Clean air ppt
Propane	235±121	123±21
i-butane	72±178	34.3±8
n-butane	86±93	42.7±11
i-pentane	97±278	40±14
n-pentane	36±64	17±4
Benzene	101±56	50±14
Chloromethane	588±104	537±38
Dichloromethane	32±23	25±3
Chloroform	14±3	11±1
Methyl-chloroform	40±7	33.9±0.4
CCl_4	93±7	92±2
Bromomethane	12±3	15±3
CFC-12	530±18	507±8
CFC-113	82±7	76.2±0.8
CFC-114	13.4±0.5	12.8±0.2
HCFC-22	158±25	140±9
HCFC-142b	16±3	15.1±0.5

Values are reported as geometric means (to minimize skew errors of a non-normal distribution) with ± one standard deviation.

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3, 1893–1923, 2003

Table 2. Total NMVOC emissions in kt NMVOC in EDGAR database, except for biofuel and biomass burning emissions (source: V2.0, Olivier et al., 1996; V3.2, Olivier et Berdowski, 2001)

	V2.0 (1990)	V3.2 (1990)	V3.2 (1995)
Greece	244	291	312
Turkey	983	559	643
Ukraine	1980	7548	6736

Table 3. Butane[a]/propane[b] and pentane[c]/propane[b] ratios at the emission point (EDGAR database, Olivier et al., 1996), after chemical processing (see text) and observed at Finokalia

		Source	After 24 h	After 48 h	Finokalia
Greece	butane/propane	4.4	3.0	2.0	0.7±0.2
	pentane/propane	5.5	2.1	0.8	0.4±0.2
Turkey	butane/propane	1.7	1.2	0.8	0.7±0.2
	pentane/propane	2.0	0.8	0.3	0.4±0.2
Ukraine	butane/propane	1.6	1.0	0.7	0.7±0.2
	pentane/propane	1.6	0.6	0.2	0.4±0.2

[a] k_{OH} = 2.26 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, Donahue et al. (1998)
[b] k_{OH} = 1.09 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, Donahue et al. (1998)
[c] k_{OH} = 3.92 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, Donahue et al. (1998), Baulch et al. (1986).

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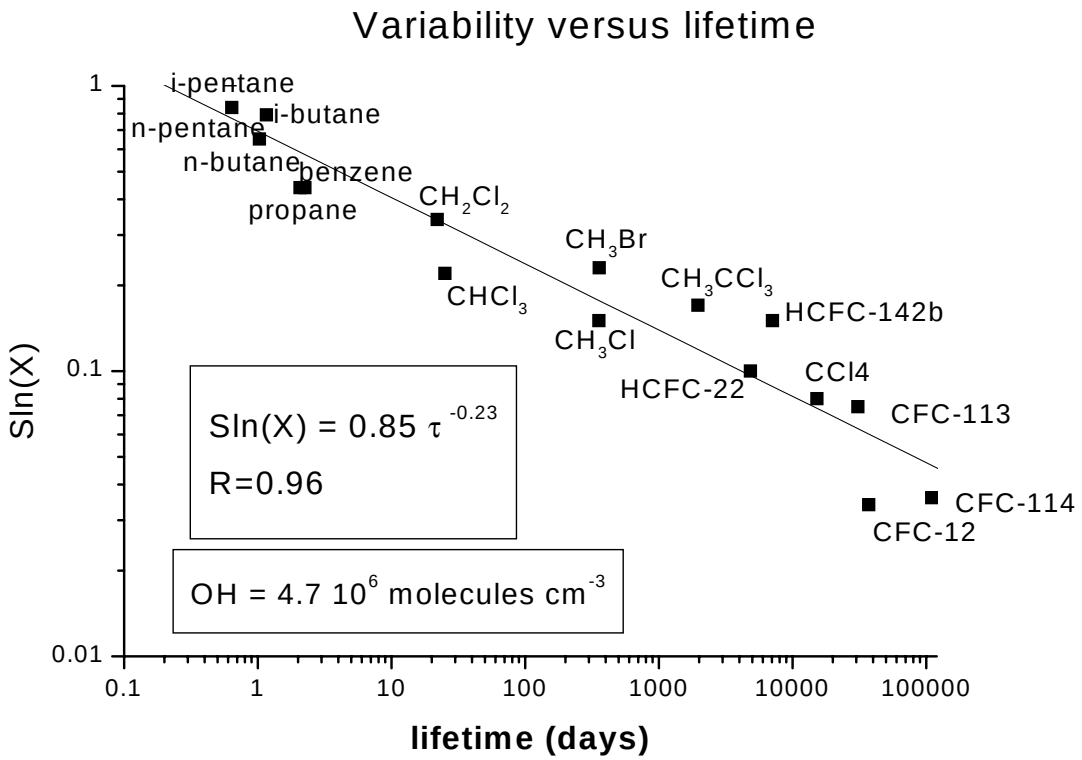

Fig. 1. Variability (standard deviation of ln mixing ratio) against lifetime for the VOC measured during the MINOS campaign.

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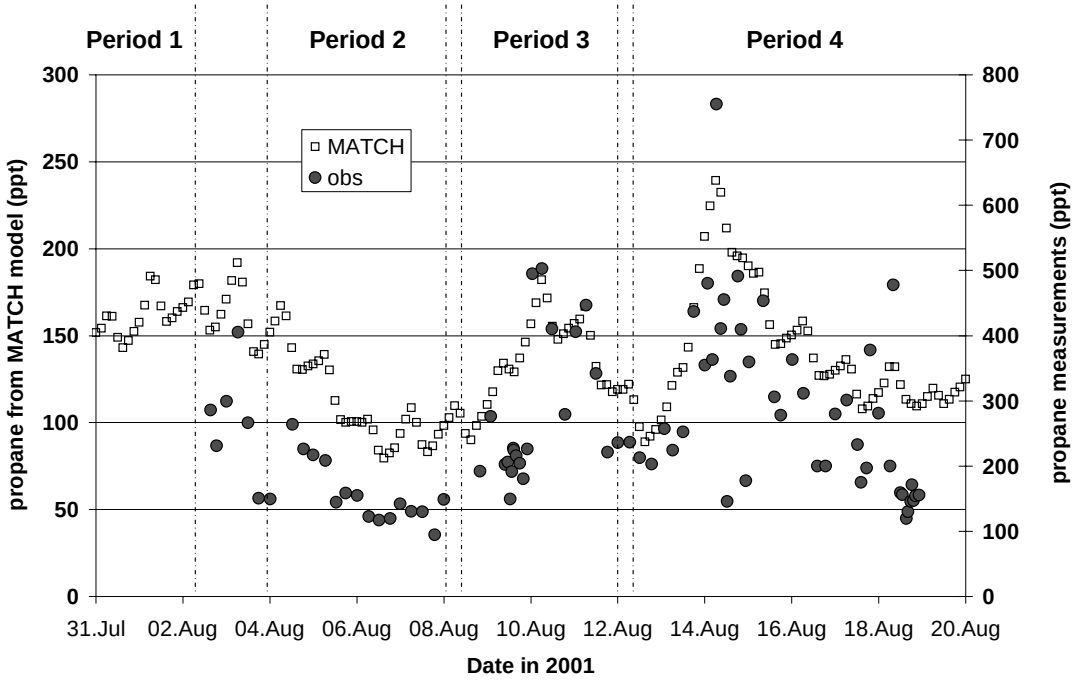

Fig. 2. Propane measurements during MINOS (closed circles) and propane calculations from MATCH (open squares). See text for the definition of periods.

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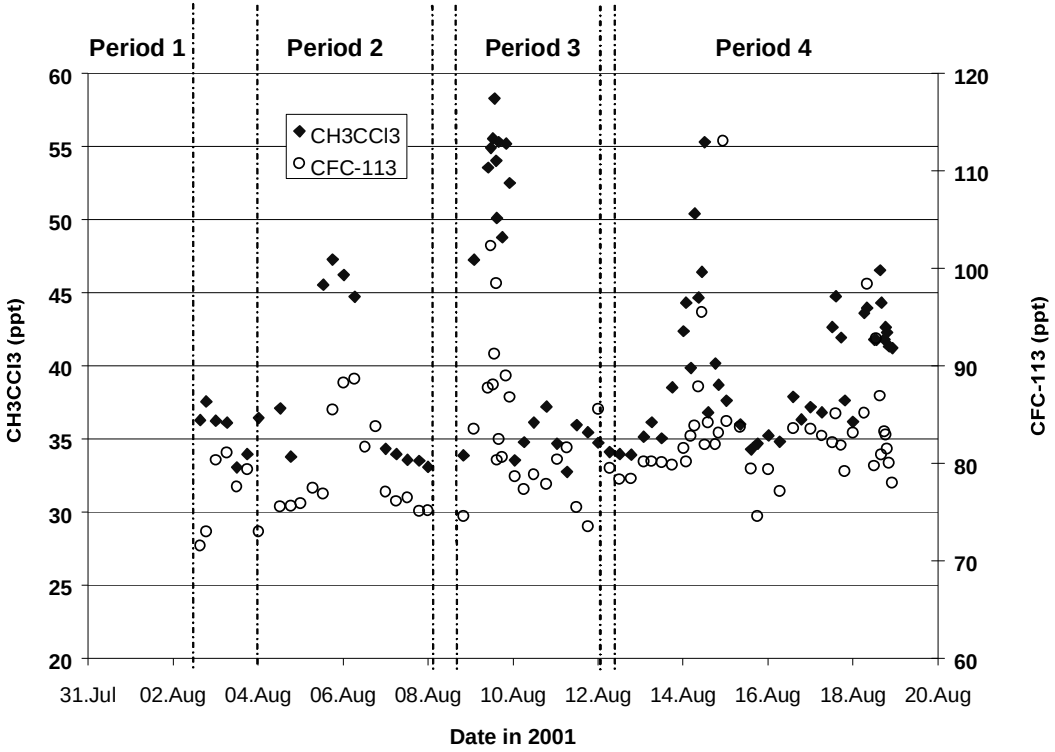

Fig. 3. Methyl chloroform and CFC-113 mixing ratios during MINOS.

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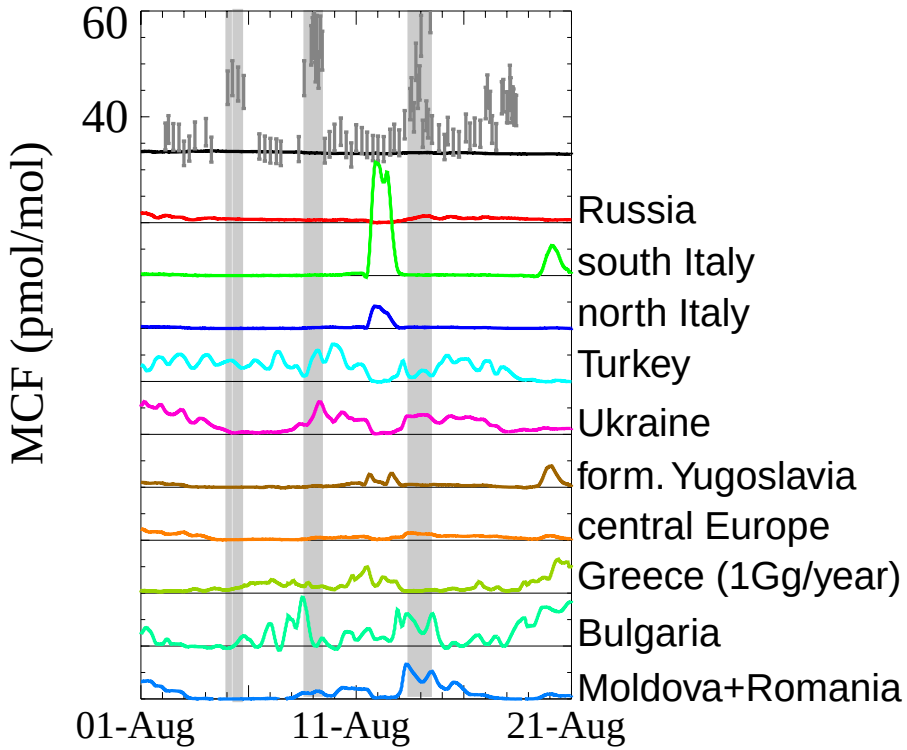

Fig. 4. Sensitivity simulations for methyl chloroform emissions for different European regions (see text for details).

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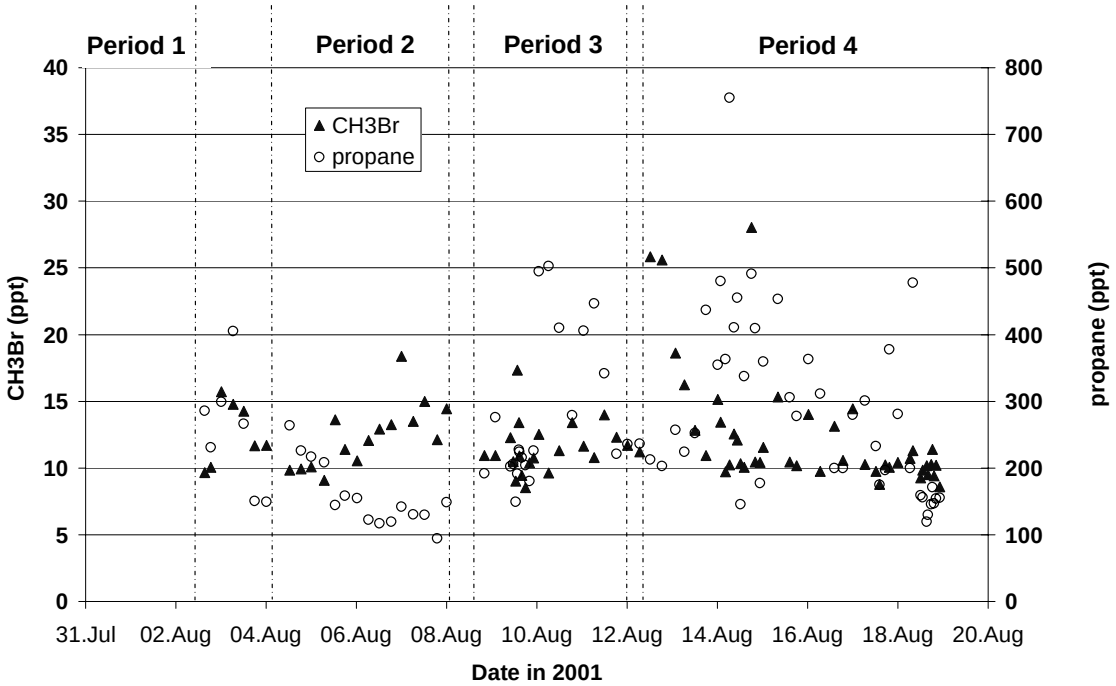

Fig. 5. Bromomethane and propane mixing ratios during MINOS.

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